

PATENT SPECIFICATION

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(54) PROCESS FOR THE MANUFACTURE OF UNSATURATED ESTERS OF CARBOXYLIC ACIDS

(71) We, KNAPSACK AKTIENGESellschaft, a body corporate organised under the laws of Germany, of 5033 Knapsack bei Köln, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known that unsaturated carboxylic acid esters can be produced by reacting an olefinic compound having from 2 to 20 carbon atoms and an aliphatic or aromatic carboxylic acid having from 2 to 20 carbon atoms with molecular oxygen or air in the gas phase and in contact with a carrier catalyst containing metallic palladium. The carrier catalyst may also contain one or more activator metals, for example, copper, gold, zinc, cadmium, tin, lead, manganese, chromium, molybdenum, tungsten, uranium, iron, cobalt, nickel, niobium, vanadium or tantalum. It is also known that these carrier catalysts can be used in further combination with one or more alkali metal or alkaline earth metal carboxylates or compounds (for example hydroxides or carbonates) yielding alkali metal or alkaline earth metal carboxylates under the reaction conditions, which are added to further improve the catalysts' activity. Thus, for example, it has been found that catalysts free from alkali metal acetate used for the reaction of ethylene acetic acid and oxygen have an activity as low as between 5 and 10 grams vinyl acetate per liter of catalyst per hour, whereas the same catalysts which, however, have between 1.5 and 5 weight percent alkali therein, produce more than 150 grams vinyl acetate per liter of catalyst per hour. The same is true concerning the production of unsaturated carboxylic acid esters having a larger number of carbon atoms. In all of

the catalysts used heretofore, the alkali metal carboxylate content therein was established by impregnating the catalyst with an alkali metal salt solution, prior to using it. However, these catalysts often have the strange property of initially promoting the combustion of ethylene to carbon dioxide, as a result of too high an activity peak which is reached promptly after the catalysts are put to use.

It has now been found that the impregnation with one or more alkali metal compounds and the subsequent drying of the catalyst, prior to using it, can be avoided by effecting the alkali impregnation during operation in the gas phase, for example, by the process reported in Belgian Patent No. 706,355. The proportion of alkali metal compound useful or needed for catalyst impregnation can also be supplied in solid form through a dosing means and during operation, the catalyst being placed in a reactor, which preferably is a fluidized bed reactor. Each of these two possibilities avoid the need to impregnate and subsequently dry the catalyst, prior to using it, and more particularly enable the initial catalyst activity to be slowly increased consistently with the quantity of alkali metal compound supplied together with the gas stream or through the dosing means. This is advantageous and prevents the temperature from "running away" as a result of too high an activity of the catalyst.

The catalyst which is free from alkali before it is put to use may contain, for example, between 0.1 and 6 weight percent, preferably between 0.5 and 2 weight percent, palladium and between 0.01 and 5 weight percent, preferably 0.1 and 2 weight percent, gold on a carrier. With reference to a continuously operated plant for the production of unsaturated esters of carboxylic acids in the gas phase: following

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the establishment of an optimum catalyst activity by the introduction described hereinabove of one or more alkali metal carboxylates into the reaction zone having the carrier catalyst placed therein, which then contains, for example, between 0.1 and 20 weight percent, preferably between 0.5 and 10 weight percent alkali metal in the form of carboxylates, it is imperative for the reaction zone to be supplied with solid or vaporous alkali metal carboxylates in an average quantity which is just sufficient to replace the quantity of carboxylates that issue in vapor form from the reaction zone. This is done in order to ensure optimum results over the whole operation period.

The present invention relates more particularly to a process for the manufacture of unsaturated esters of carboxylic acids by reacting an olefinic compound having from 2 to 20 carbon atoms and an aliphatic or aromatic carboxylic acid having from 2 to 20 carbon atoms with molecular oxygen or air in the gas phase, if desired in the presence of one or more inert gases, at temperatures of between 100 and 250°C, preferably between 150 and 220°C, under pressures between 1 and 21 atmospheres absolute, preferably between 5 and 11 atmospheres absolute, in contact with a catalyst consisting of metallic palladium, a carrier and optionally a further activator metal, which comprises supplying the alkali metal-free-catalyst, in a first step and during operation, with one or more alkali metal carboxylates or compounds yielding alkali metal carboxylates under the reaction conditions, the said alkali metal carboxylates or compounds being supplied in the quantity necessary to effect catalyst activation, and, following establishment of an optimum catalyst activity, supplying the alkali metal carboxylate-saturated catalyst, in a second step, with a further quantity of alkali metal compound, the said further quantity of alkali metal compound being normally just sufficient to replace the loss of alkali metal carboxylates occasioned by evaporation from the hot catalyst.

To this effect, the gas mixture to be passed over the catalyst may be used in combination with one or more alkali metal compounds. It is also possible to supply the reaction zone having the catalyst placed therein with one or more solid alkali metal components, through a dosing means. The alkali metal compound may be dissolved in the carboxylic acid which is to be added in measured quantities, and which is to undergo evaporation. With reference to the second process step, it is advantageous to establish an alkali metal concentration corresponding to the quantity of alkali metal carboxylate which is contained in the condensate coming from the furnace and hav-

ing the carboxylic acid and unsaturated carboxylic acid ester therein. The carboxylic acid to be introduced may be evaporated in conventional manner in a carboxylic acid-evaporation zone and the alkali metal compound may be introduced thereto. It is also possible to introduce the olefinic compound and molecular oxygen or air into the carboxylic acid-evaporation zone having the alkali metal compound therein. The olefinic compound, carboxylic acid in vapor form and molecular oxygen or air may be passed through or over a shell heated to a temperature of between 100 and 250°C, preferably between 150 and 220°C, and containing the alkali metal compound deposited on a carrier. Following this, the gas mixture enriched in vaporous alkali metal carboxylate is conveyed to the catalyst-containing reaction zone. Shells which may be found to have been used-up by evaporation of alkali metal carboxylate can be regenerated by spraying a solution of alkali metal carboxylate in carboxylic acid thereonto.

The useful olefinic compounds having from 2 to 20, preferably from 2 to 10 carbon atoms, include, for example, aliphatic or cycloaliphatic olefins or diolefins, particularly ethylene, propylene, butene, butadiene, pentene, cyclopentadiene, cyclohexene or cyclohexadiene, and the useful carboxylic acids having from 2 to 20, preferably from 2 to 10 carbon atoms include, for example, acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, lauric acid, palmitic acid, stearic acid or benzoic acid. The unsaturated esters of the carboxylic acids contain altogether between 4 and 40, preferably between 4 and 20 carbon atoms. Useful catalyst activators are, for example, the metals specified in the opening paragraph hereinabove, and the useful catalyst carriers preferably include silicic acid (SiO_2), kieselguhr, diatomaceous earth, aluminum oxide, aluminum silicate, aluminum phosphate, pumice, asbestos, silicon carbide or active carbon.

The following Examples illustrate the process of the present invention:

EXAMPLE 1: (Comparative Example)

1 kg (= 1.85 liter) of a ball-shaped or spheroidal silicic acid carrier (balls 5 to 6 mm in diameter) was mixed and thoroughly impregnated with a solution containing 11 grams noble metal ions, namely 8 grams Pd^{++} in the form of PdCl_2 and 3 grams Au^{+++} in the form of HAuCl_4 . The whole was dried with agitation to ensure uniform distribution of the noble metal salts on the carrier. The dry mass was introduced into a 5% aqueous hydrazine hydrate solution. Following complete reduction of the noble metal compounds to the corresponding

noble metals, supernatant liquid was poured off, the whole was thoroughly washed with distilled water and dried under vacuum at 60°C. The alkali free-catalyst so produced was ready for use without awaiting further treatment. It contained per liter 5.95 grams noble metals or about 0.7 weight percent Pd and 0.26 weight percent Au.

1380 normal liters/hr (measured at S.T.P.) of a feed gas composed of 16.3% by volume acetic acid, 23.2% by volume nitrogen, 6.1% by volume oxygen and 54.4% by volume ethylene were conveyed in a single passage reaction at 180°C and under a pressure of 6 atmospheres absolute over 1000 milliliters of the catalyst so prepared, which was placed in a reactor 32 mm in diameter and 2 meters long. The velocity of flow was 13 cm/second and the contact time 9.6 seconds. The reaction gas was condensed to eliminate the reaction products therefrom. 600 grams/hr condensate containing 1 weight percent vinyl acetate were obtained. The average catalyst activity was found to be 6 grams vinyl acetate per litre of catalyst per hour. Vinyl acetate was obtained in a yield of 90% based on the 0.23% ethylene conversion rate.

EXAMPLE 2:

A gas mixture with the composition reported in Example 1 was passed at the same rate and under the conditions described in Example 1 over 1000 milliliters catalyst the same as than used in Example 1, save that a shell heated to 180°C was placed in

the gas stream path, ahead of the reactor. The shell used for effecting alkali impregnation of the catalyst contained a mixture comprising 15 grams potassium acetate and 15 grams sodium acetate deposited on 250 grams silicic acid carrier, and was exchanged initially at 7 day intervals. The activity of the catalyst was found to rapidly increase promptly after it was put to use.

Operation period days	Catalyst activity in grams vinyl acetate per liter per hour
1	26
2	34
3	45
7	62
11	103
13	121
17	139
23	172
29	185
33	185

After 33 days of operation, the process was found to be in equilibrium and 675 grams/hr condensate containing 27.5 weight percent vinyl acetate were obtained.

During the operation period, the condensates were tested as to the alkali contained therein. It was found that the alkali metal acetate evaporating from the alkali-containing shell initially was completely adsorbed by the catalyst. The following values were determined:

Operation period days	Alkali metal contained in furnace condensates in parts per million Na ⁺	K ⁺	Catalyst activity in grams vinyl acetate per liter per hour
1	0	0	26
9	<0.1	<0.1	83
13	<0.1	<0.1	121
17	<0.5	<0.1	139
23	0.8	0.5	172
29	11.3	0.7	185
33	15	7	185

From the 30th day of operation on, the shell was exchanged at such intervals that alkali metal acetate was delivered from the shell ahead of the reactor to the catalyst in quantities consistent with the loss of alkali metal acetates occasioned by evaporation from the hot carrier catalyst. From now on vinyl acetate was obtained in a yield of 91%, based on an ethylene conversion rate of 7.1%.

EXAMPLE 3: (Comparative Example)

1.8 cubic meters/hr feed gas composed

of 61.2% by volume ethylene, 20.5% by volume acetic acid, 6.6% by volume oxygen and 11.7% by volume CO₂ were passed at an inlet pressure of 8 atmospheres absolute and a reaction temperature of 200°C through a catalyst furnace 2.8 meters long, which formed part of a commercial cycle system and contained 2 liters catalyst with the composition indicated in Example 1. The contact time was 4 seconds, the gas load 4.16 normal cubic meters per liter of catalyst per hour, and the velocity of flow 70 cm/second. The

reaction gas was condensed (4560 grams/hr condensate containing 0.44 weight percent vinyl acetate) to eliminate the reaction products therefrom, and unreacted acetic acid was recovered and recycled, after addition of ethylene and oxygen to replace the ethylene and oxygen transformed. Vinyl acetate was obtained in a yield of 88%, based on an ethylene conversion rate of 0.12%. The catalyst was found to have an activity of 10 grams vinyl acetate per liter per hour.

EXAMPLE 4:

A gas mixture having the composition indicated in Example 3 was passed at the same rate and under the conditions reported in that Example over 2 liters catalyst with the composition specified in Example 1. In contrast with Example 3, a shell heated to 200°C was placed in the gas stream path, ahead of the reactor. The shell used for effecting alkali impregnation of the catalyst contained a mixture comprising 80 grams potassium acetate and 20 grams sodium acetate deposited on 500 grams silicic acid carrier. The shell was initially exchanged at intervals of 4 days until the loss of alkali occasioned by evaporation from the hot carrier catalyst and the supply of alkali to the catalyst were found to be consistent with one another. From that time on there were obtained 5070 grams/hr condensate containing 18.8 weight percent vinyl acetate, 12 parts per million Na^+ and 7 parts per million K^+ . In other words, substantially 60 milligrams Na^+ and 35 milligrams K^+ were found to evaporate per hour from the catalyst. From now on the shells were exchanged at such intervals that the loss of alkali metal acetate occasioned by evaporation from the hot catalyst was just compensated. Vinyl acetate was obtained in a yield of 89.5%, based on ethylene conversion rate of 5.5%. The catalyst was found to have an activity of 475 grams vinyl acetate per liter of catalyst per hour.

The same result was obtained in those cases in which a dosing means delivering the alkali metal acetates in solid form to the catalyst was substituted for a shell having the alkali metal acetates therein.

EXAMPLE 5: (Comparative Example)

1350 grams (= 3 liters) of a particulate silicic acid carrier (particle size between 0.1 and 0.2 mm) were mixed and thoroughly impregnated with an aqueous solution containing 21.6 grams noble metal ions, namely 16.1 grams Pd^{++} in the form of PdCl_2 and 5.5 grams Au^{+++} in the form of HAuCl_4 . The solution contained a quantity of water just sufficient to permit absorption by the carrier. The mass was subsequently dried

in a stream of nitrogen, and the dry mass was introduced into an aqueous hydrazine solution to effect reduction of the noble metal compounds deposited on the carrier to the corresponding noble metals. Following complete reduction, the catalyst mass was thoroughly washed with water and dried under reduced pressure. The alkali free-catalyst so produced was ready for use without awaiting further treatment. It contained per liter 7.32 grams noble metals or substantially 1 weight percent Pd and 0.4 weight percent Au. 2.5 liters of the catalyst so produced were placed in a fluidized bed reactor, which was a steam-heated, stainless steel tube 3 meters long with an internal diameter of 50 mm.

10 normal cubic meters/hr of a gas composed of 64% by volume ethylene, 16% by volume acetic acid, 8% by volume oxygen and 12% by volume CO_2 were passed at a reaction temperature of 188°C and under a pressure of 8 atmospheres absolute over the 2.5 liters catalyst. The velocity of flow of the gas mixture was 34 cm/second, the contact time was 4.1 seconds, based on the apparent volume (2.5 liters) of the catalyst, and the gas load was 4 normal cubic meters per liter of catalyst per hour.

The reaction products were eliminated from the reaction gas in conventional manner. 4375 grams/hr condensate containing 1.8 weight percent vinyl acetate were obtained. The catalyst was found to have an activity of 32 grams vinyl acetate per liter of catalyst per hour. Vinyl acetate was obtained in a yield of 89%, based on an ethylene conversion rate of 0.36%.

EXAMPLE 6:

A gas mixture having the composition indicated in Example 5 was passed at the same rate and under the conditions reported in that Example over 2.5 liters of the catalyst used therein. In contrast with Example 5, a dosing means was used to deliver, during operation, 85 grams potassium acetate to the catalyst, promptly after it was put to use. Already after 8 hours of operation, the catalyst activity was found to be 950 grams vinyl acetate per liter of catalyst per hour. From that time on there were obtained 5650 grams/hr condensate containing 42 weight percent vinyl acetate and 12 parts per million K^+ . In other words, substantially 62 milligrams K^+ in the form of acetate (= 1.63 grams/day) were found to evaporate from the hot carrier catalyst. Vinyl acetate was obtained in a yield of 90%, based on an ethylene conversion rate of 10.5%.

As the experiment went on, the dosing means was used to deliver alkali metal acetate to the catalyst in quantities just sufficient to compensate the loss of alkali metal

acetate occasioned by evaporation from the hot carrier catalyst. To this effect, the 2.5 liters catalyst were fed during operation with a daily quantity of 4.15 grams potassium acetate, through the dosing means.

EXAMPLE 7:

10 cubic meters/hr of a gas composed of 64% by volume ethylene, 16% by volume propionic acid, 8% by volume oxygen and 12% by volume CO₂ were passed under a pressure of 8 atmospheres absolute and at 190°C over 2.5 liters of the catalyst described in Example 5, placed in the fluidized bed reactor. The velocity of flow of the gas mixture was 34 cm/second, the contact time was 4.1 seconds, based on the apparent volume of the catalyst, and the gas load was 4.0 normal cubic meters per liter of catalyst per hour. Promptly after the apparatus was put to use, the catalyst was fed during operation with 100 grams potassium propionate, through a dosing means. Already after 10 hours, the catalyst was found to have an activity of 900 grams vinyl propionate per liter of catalyst per hour. From that time on there were obtained 6300 grams/hr condensate containing 35.8 weight percent vinyl propionate and 8 parts per million K⁺. In other words, substantially 50 milligrams K⁺ in the form of propionate (1.21 grams/day) evaporated from the hot catalyst. Vinyl propionate was obtained in a yield of 91%, based on an ethylene conversion rate of 8.5%.

As the experiment went on, the dosing means was used to deliver potassium propionate to the catalyst in quantities just sufficient to compensate the loss of propionate occasioned by evaporation from the hot carrier catalyst.

EXAMPLE 8:

10 normal cubic meters/hr of a gas composed of 65% by volume ethylene, 15% by volume isobutyric acid, 8% by volume oxygen and 12% by volume CO₂ were passed over the catalyst under the conditions reported in Example 7. Promptly after the start of the experiment, the catalyst was fed through a dosing means with a mixture of 85 grams potassium acetate and 15 grams sodium acetate, which underwent transformation into the corresponding isobutyrate, during operation. Already after some hours, the catalyst was found to have an activity of 500 grams vinyl isobutyrate per liter of catalyst per hour. From that time on there were obtained 6925 grams/hr condensate containing 18 weight percent vinyl isobutyrate, 10 parts per million N⁺ and 6 parts per million K⁺. In other words, substantially 69 milligrams/hr Na⁺ and 41.5 milligrams/hr K⁺ in the form of iso-

butyrates (= 1.65 grams/day Na⁺ and 1 gram/day K⁺) were found to evaporate from the hot catalyst. The loss of alkali metal isobutyrate occasioned by evaporation from the hot carrier catalyst was compensated by the supply of substantially identical quantities of alkali metal acetate, through the dosing means. Vinyl isobutyrate was obtained in a yield of 90% based on an ethylene conversion rate of 4.1%.

EXAMPLE 9:

10 normal cubic meters/hr of a feed gas mixture composed of 60% by volume propylene, 18% by volume acetic acid, 8.2% by volume oxygen and 13.8% by volume CO₂ were passed over the catalyst, under the conditions reported in Example 7. Promptly after the start of the experiment, the catalyst was fed during operation with 85 grams potassium acetate, through a dosing means. Within a few hours, the catalyst was found to have an activity of 450 grams allyl acetate per liter of catalyst per hour. From that time on there were obtained 5550 grams/hr condensate containing 20.2 weight percent allyl acetate and 11 parts per million K⁺. In other words, substantially 61 milligrams K⁺ in the form of acetate (= 1.46 grams/day K⁺) were found to evaporate from the hot catalyst. Fresh potassium acetate was delivered to the catalyst through a dosing means at the same rate as potassium acetate evaporated from the hot carrier catalyst. Allyl acetate was obtained in a yield of 85%, based on a propylene conversion rate of 4.8%.

WHAT WE CLAIM IS:—

1. A process for the manufacture of unsaturated esters of carboxylic acids by reacting an olefinic compound having from 2 to 20 carbon atoms and an aliphatic or aromatic carboxylic acid having from 2 to 20 carbon atoms with molecular oxygen or air in the gas phase, if desired in the presence of one or more inert gases, at temperatures between 100 and 250°C, under pressures between 1 and 21 atmospheres absolute, in contact with a catalyst consisting of metallic palladium, a carrier and optionally a further activator metal, which comprises supplying the alkali metal-free catalyst, in a first step and during operation, with one or more alkali metal carboxylates or compounds yielding alkali carboxylates under the reaction conditions, the said alkali metal carboxylates or compounds being supplied in the quantity necessary to effect catalyst activation, and, following establishment of an optimum catalyst activity, supplying the alkali metal carboxylate-saturated catalyst, in a second step, with a further quantity of alkali metal compound, the said further quantity of

alkali metal compound being normally just sufficient to replace the loss of alkali metal carboxylates occasioned by evaporation from the hot catalyst.

5 2. A process as claimed in claim 1, wherein the said temperatures are between 150 and 220°C.

3. A process as claimed in claim 1 or 2, wherein the said pressures are between 5 and 11 atmospheres absolute.

10 4. A process according to claim 1, 2 or 3, wherein the gas mixture to be passed over the catalyst is used in combination with one or more alkali metal compounds.

15 5. A process as claimed in claim 1, 2 or 3, wherein the reaction zone having the catalyst placed therein is supplied with one or more solid alkali metal compounds, through a dosing means.

20 6. A process as claimed in claim 1, 2, 3 or 4, which comprises dissolving the alkali metal compound in the carboxylic acid which is to be added in measured quantities and which is to undergo evaporation, and establishing for use in the second step, an alkali metal concentration corresponding to the quantity of alkali metal carboxylate contained in the furnace condensate having the carboxylic acid and unsaturated carboxylic acid ester therein.

30 7. A process as claimed in claim 1, 2, 3 or 4, wherein the carboxylic acid to be added is evaporated in conventional manner in a carboxylic acid-evaporation zone receiving the alkali metal compound.

35 8. A process as claimed in claim 7, wherein the olefinic compound and molecular oxygen or air are additionally intro-

duced into the carboxylic acid-evaporation zone having the alkali metal compound therein. 40

9. A process as claimed in claim 1, 2, 3 or 4, wherein the olefinic compound, carboxylic acid in vapor form and molecular oxygen or air are passed through or a shell heated to a temperature of between 100 and 250°C, and containing the alkali metal compound deposited on a carrier, and wherein the gas mixture enriched with alkali metal carboxylate in vapor form is conveyed to the reaction zone having the catalyst placed therein. 45

10. A process as claimed in claim 9, wherein the shell is heated to a temperature of between 150 and 220°C. 50

11. A process as claimed in claim 9 or 10, wherein spent shells such as those used-up by evaporation of alkali metal carboxylate are regenerated by spraying a solution of alkali metal carboxylate in carboxylic acid thereonto. 55

12. A process for the manufacture of unsaturated esters of carboxylic acids conducted substantially as described in any Examples 2, 4 and 6 to 9 herein. 60

13. Unsaturated esters of carboxylic acids whenever obtained by a process as claimed in any one of claims 1 to 12. 65

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